An Innovative Breakthrough in Automated ATR Sampling

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Automating spectroscopic sampling delivers benefits to chemists and laboratory technicians by speeding the development of routine calibrations, reducing monotonous tasks and increasing efficiency and output. It also proves to be a valuable tool for management when used to facilitate training and to track multiple users. Automation minimises sampling and reporting errors, and aids in time and data management. All increase the return on investment.

Certain spectroscopic sampling techniques adapt more readily to automation. These include diffuse and specular reflection, and transmission. Samples for automated diffuse measurements are often powders. Typical applications requiring high-throughput sampling for large-scale studies are infrared (IR) analysis of soil and minerals and for routine testing, the IR analysis of kidney stones. However, this technique is not exclusively for powders. IR automated diffuse measurements have been applied to gemstone analysis including the evaluation of diamond quality. When working with intractable solid samples, the abrasion technique is suitable for high-throughput, automated measurements. The abrasion disk is simply rubbed against the sample, removed from its holder and placed directly on a multi-position sample plate for measurement in a diffuse reflection accessory.

For specular reflection applications, the goal is often to measure reflectivity of a sample at a prescribed point(s) using a holder to accommodate numerous samples on a single platform or to map a larger surface such as a silicon wafer. Automation has also been applied to a variable angle specular reflection accessory to allow spectra to be collected at a range of angles thus eliminating substitution errors resulting from removing the sample between background and sample measurements.

Automated transmission has been employed for solids that transmit over the spectral range of interest and is of an appropriate pathlength to produce a quality spectrum. Example applications include measurements of lenses and silicon wafers. Automated liquid transmission sampling accessories use a transmission cell and require a sophisticated sample delivery and flushing system. Various automated diffuse and specular reflection and transmission accessories are available from PIKE Technologies (Madison, WI).

Until now, an automated attenuated total reflection (ATR) accessory on a non-micro scale has been elusive despite ATR being the most popular mid-IR sampling technique due to its ease-of-use and small fixed pathlength. The primary advantage of FTIR-ATR measurements is minimal sample preparation. However, cleaning of the ATR crystal after every measurement is mandatory and has hindered the development of a commercial automated ATR in the past. With new innovations these challenges have been met and the advantages of automation are realised with the introduction of the AutoATR by PIKE Technologies. This new sampling accessory greatly enhances productivity of large-scale studies and facilitates routine measurements for high-throughput labs. The accessory is suitable for making ATR measurements of liquids, gels, pastes, casted films and more.

AutoATR Technology and Design

The AutoATR merges an exciting new ATR crystal developed via microtechnology with a microtiter plate platform offering precision mechanics and automated software control. Using a 24-well microtiter plate format enables 24 unique ATR measurements to be conducted within one run. At the heart of this accessory is the IRUBIS ATR crystal (IRUBIS GmbH, Munich, Germany). These single reflection ATR crystals are made from 500-µm thick silicon functionalised with multiple microprisms, which couples the light into the crystal (Figure 1). The dimensions of an individual crystal are 9 mm x 11 mm; the ATR active area is 7 mm x 9 mm. Each 24-well plate consists of 24 individual and removable Si ATR crystals. The microplate has a two-piece design. Crystals are seated in the immersions located in the bottom portion. The upper portion, made from PTFE for inertness, contains machined sample wells. An expanded PTFE seal provides a leak-proof union. The 24-well ATR plate is easily disassembled to remove the crystal if necessary.

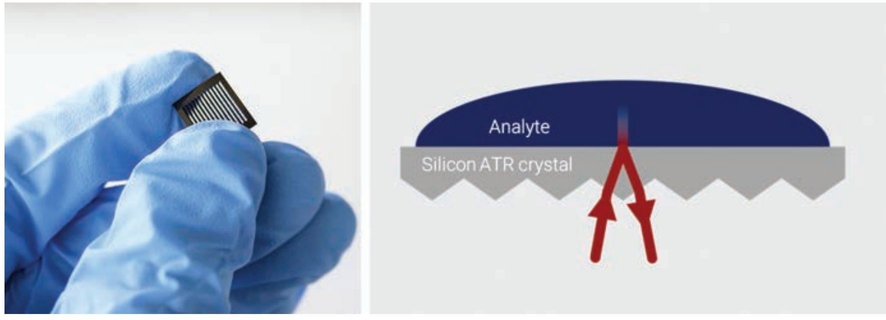

Figure 1. IRUBIS Si ATR crystal.

Silicon, in this thin 500-µm form, is an ideal multipurpose ATR element. It has an extremely inert sampling surface and is suitable for use with substances having a pH between 1-12. The changeable ATR crystals also offer the opportunity to store the samples and to prepare different samples at the same time (i.e. drying). In addition, the plain silicon surface may be functionalised outside the microplate, because the crystals are removable and interchangeable.

The AutoATR is designed to fit into the sample compartment of most FTIR spectrometers. Its X,Y tray moves to a position outside the accessory for easy loading and unloading of samples while maintaining purge. The stage is driven by precision servo motors with optical encoders for speed and reproducibility. USB and DC power are the only external connections required. The optical design is based upon a precision ellipsoidal reflector, which has been diamond turned for optimal performance. The optics demagnify the beam to a size that fills the active ATR area.

The accessory's control software, AutoPRO, plays an integral role in its usability and value. Data collection is enabled through communication with most FTIR software programs. It allows for traceability by facilitating multiple users. Sample descriptions may be entered manually or uploaded from a spreadsheet; sample information is stored with the spectral file. For ease of file finding, the program offers numerous file naming schemes such as time stamp or unique file prefix naming. It also incorporates options for calling macros to execute post-processing commands such as peak picking, report generation and exporting data to a spreadsheet format.

AutoATR Performance

For traditional Si ATR crystals, the beam pathlength through the crystal is several millimeters in some cases, which results in complete absorption of the Si phonon bands in the fingerprint region (1500 – 400 cm^{-1}). The beam pathlength through the thin profile of the IRUBIS Si ATR element minimises absorption from Si phonon bands and offers a full mid-IR spectral range (5000 – 400 cm^{-1}). The absorbance is comparable to a standard diamond ATR. Figure 2 shows spectra of oil collected using the AutoATR versus a single reflection diamond ATR. Absorbance band position, shape and magnitude are very similar. The efficiency of the accessory's delivery optics and Si ATR element coupled with several microprisms results in high energy throughput and reproducibility. Thus, high-quality spectra may be collected over a short time period.

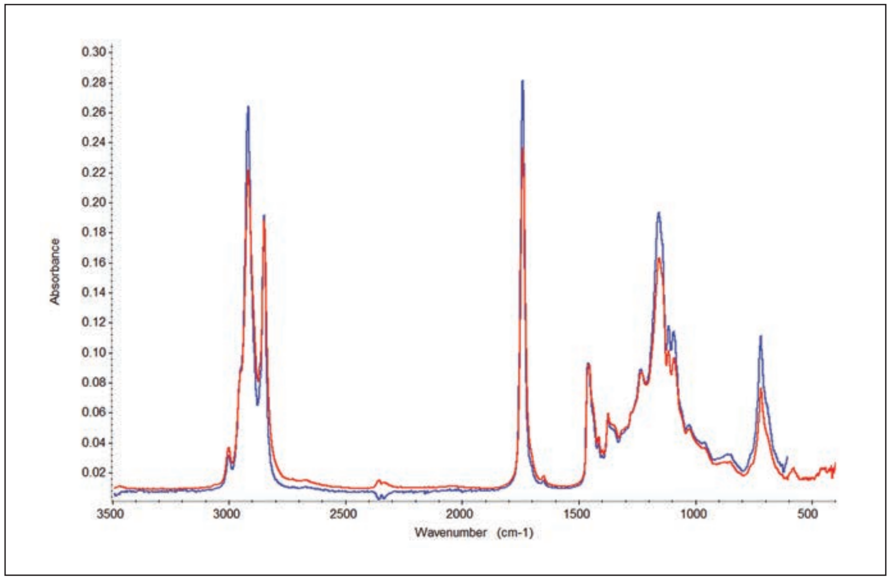

Figure 2. Spectra of oil collected using the AutoATR (red) and a single reflection diamond ATR (blue).

AutoATR Applications

One of the applications the AutoATR high-throughput accessory targets is comprehensive larger studies. Fields of biology [1,2,3], medical, pharmaceutical and food [4,5] could benefit from an automated ATR. For example, the analysis of blood samples by Fourier transform infrared spectroscopy to detect diseases like cancer [6,7] or malaria [8] is a research area of interest spanning the last decade and continues today. For studies where hygienic issues are of concern the ATR crystals and the plate can be easily cleaned, disinfected and reused. Additionally, there are ongoing efforts to transfer infrared spectroscopy from academic research into clinics. Therefore, large spectral databases for machine learning and calibration algorithms are needed. An automated ATR high-throughput device fulfils this requirement and enables larger studies, while increasing lab efficiency and minimising workforce requirements.

The AutoATR could be a useful tool for monitoring bioreactors. The main benefit would be cost savings because parameters like glucose, acetate, lactate or protein quantitation can be determined using one automated FTIR method that does not need consumables.

In the food industry, IR techniques are adopted for the routine analysis of milk and other beverages like wine and juices [9,10]. Using the AutoATR, costs per measurement would decrease, which in turn could improve the overall quality of these beverages. For example the automated transmission measurement of honey and sparkling wine, until now, was very difficult. In contrast, ATR mode offers easy measuring of samples with high viscosity and high amounts of dissolved gas. Transmission cells can clog; however, when making measurements via ATR samples are simply deposited on top of the crystal.

Applications in the chemical industry include the analysis of lubricants [11]. The condition monitoring of lubricants using FTIR helps to determine whether a lubricant needs to be replaced. Current automated FTIR systems are based on transmission mode and require an elaborate automated flow-cell system. The overall technical complexity could be reduced by using the AutoATR, directly resulting in increased reliability and decreased investment costs.

Conclusions

Due to technological innovations and creativity, automated ATR sampling is now possible. Thin-profile Si ATR crystals coupled with microprisms are integrated into a 24-well microplate format. Using the ATR microplate within an automated X,Y stage allows for spectra of 24 individual samples to be collected. Laboratory environments that would benefit from ATR automation would be those participating in large-scale studies and high-throughput laboratories conducting routine measurements.

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